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Combining uretdione and disulfide reversibly degradable polyurethanes: route to alternating block copolymers†

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Uretdione (temperature and catalyst controlled) and disulphide (REDOX controlled) functionalised polyurethanes have been described and the reversibility of these bonds tested . The polymers have been synthesised with reversible covalent groups present throughout their backbone developing routes to reversibly degradable polyurethanes. These materials degrade and reheal in response to different external stimuli, which supplies a proof of concept for controlling the molecular weight, and therefore, the physical properties of a polyurethane. Further, a unique route to an alternating block copolymer is also discussed that utilises a mixture of disulphide and uretdione functionalised polymers as the reagents to form a thiourethane. The dramatically reduced safety hazards of dealing with the functionalised polymers, in comparison to the free isocyanate and thiols, could be of great interest to industrial application for current drives towards safer routes to polyurethanes.

Introduction

Since their discoveries in the 19th and early 20th centuries, isocyanates and polyurethanes have grown to be amongst some of the major chemicals produced worldwide with the market growing approximately 5% year on year.[1] Polyurethanes consist of a wide range of materials (thermosets, thermoplastics, foams *etc.*) that are produced from a relatively simple selection of diisocyanates and a polyol (*e.g.* toluene diisocyante (TDI), methylene diphenyl diisocyanate (MDI)).[1-2] Important physical properties of polyurethanes arise from the phase separation of their hard and soft segments.[3] However, a major drawback in the synthesis of polyurethanes is the requirement for high toxicity isocyanates, which are in the process of being discouraged by REACH,[4-5] particularly given the 1984 Bhopal disaster.[6-7]

Reversible bonds between different functional groups have been incorporated into polymers, utilising reversible covalent,[8-11] non-covalent,[12-13] and self-healing chemistries,[14-17] which have been incorporated into polymers to provide reversibly degradable/self-healing materials.[18-22] Similar materials are now often referred to as vitrimers.[23] A reversible reaction that has been studied is the oxidation of thiols to disulphides and the reverse reaction reducing back to thiols, which has important uses in biological systems.[9] These bonds have been successfully incorporated into various reversibly crosslinked and biodegradable polymeric systems.[24-25] Du Prez has recently reported vitrimers based on the amine exchange of vinylogous urethanes[26] and has expanded this with demonstrating dynamic vinylogous urethane chemistry platform. This allows for precise control of the exchange reaction giving materials that can be processed with short relaxation times, showing only little creep at application temperature.[27] The disulfide bond can be relatively easily incorporated into polymers. This bond may then be broken by a variety of mechanisms, and the released thiols can be readily oxidised back to the disulfide. As the disulfide bond can be cleaved by a nucleophile, there are a wide range of possible reducing agents.[24] In this current work tributyl phosphine (Bu_3P)[28-29] was used due to its relative stability towards oxidation and high affinity to sulfur.[30] The reformation of the disulfide bond may also be achieved by a number of mechanisms.[24] Herein the effective and efficient oxidation by the metal catalyst iron(III) chloride ($FeCl_3$)[29] was chosen for this work.

There are various industrial products that contain blocked isocyanates, which can be deprotected at a given temperature utilising the weak reversible bonds between isocyanates and a variety of functional groups.[31-32] Below the threshold temperature, the isocyanate is in a bound form, reducing its reactivity and toxicity. Since blocked isocyanates are less sensitive to nucleophilic attack the storage lifetime of the product is also increased. The equilibrium reaction between the binding / release of the isocyanate is driven by the removal of isocyanate through further reactions and the removal of the small blocking molecule. An excellent example of a blocked isocyanate that does not use a small blocking group is an uretdione.

In addition to reacting with nucleophiles, the isocyanate functional group is capable of dimerising to form an four membered ring functional group, a uretdione.[33] Dimers of aromatic isocyanates can be formed upon the addition of a nucleophilic catalyst, such as a trialkyl phosphine.[34] Uretdiones have been described in literature since 1858 with the reported synthesis of a phenyl isocyanate dimer,[35] which involved a

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phosphine catalyst. The reaction has been shown to be controllable by quenching the phosphine catalyst with an alkylating agent such as benzyl chloride.[34] Isocyanate dimerisation/uretdione formation is an equilibrium reaction, with the conversion to dimer increasing as temperature decreases. Uretdiones are indeed relatively stable, which has been demonstrated by the TDI dimer not dissociating back to TDI monomer until it is heated to >150°C in the absence of a catalyst.[36] However, the presence of a catalyst can significantly reduce the dissociation temperature.[1] To the best of our knowledge there have been no reported studies of uretdione groups being used for the synthesis of reversibly degradable/dynamically covalent materials or of their combination with disulfide bonds.

Results and Discussion

Disulfide functional reversibly degradable polyurethanes

The reaction between hydroxyethyl disulphide and toluene diisocyanate was carried out in THF for 2 hours at 40°C, using dibutyltin dilaurate (DBTDL) as catalyst (Figure 1). This proved successful giving a polyurethane with a M_n of 12,000 g mol^{-1}.

^{1}H NMR and GPC analysis showed that the disulphide group had been successfully incorporated throughout the backbone of a polyurethane (Figure 2), and subsequently the potential cleavage of these groups through the reduction of the disulphide to thiols with tributylphosphine was examined. Upon the addition of tributylphosphine at 40°C a decrease in M_n (12,000 to 1,500 g mol^{-1}) was observed, with the majority of the polyurethane degrading (Figure 3). Although there are multiple oligomers apparent from the GPC trace, these most likely correspond to low molecular weight species (dimers, trimers *etc.* possibly being rebound through exposure to air while analysis is being carried out) with the majority of the disulphide groups having successfully been cleaved. This displays a simple

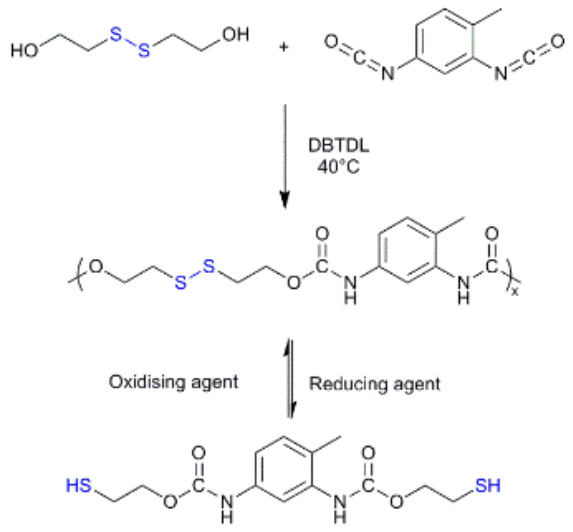

Figure 1 Synthesis of a disulphide containing polyurethane that has disulfide bonds placed throughout its backbone. The resulting polymer is degraded down to dithiols and reformed back to a polyurethane by a REDOX reaction.

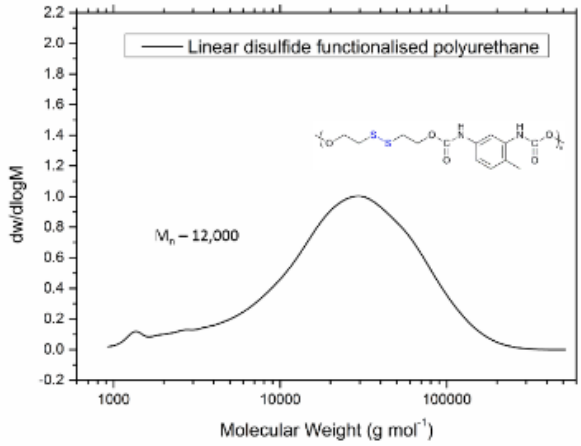

Figure 2 GPC trace of a disulphide functionalised polyurethane with reversibly cleavable groups placed throughout the backbone (linear disulfide polymer) (M_n – 12,000 g mol^{-1})

and efficient route to the synthesis of a controllably degradable polyurethane.

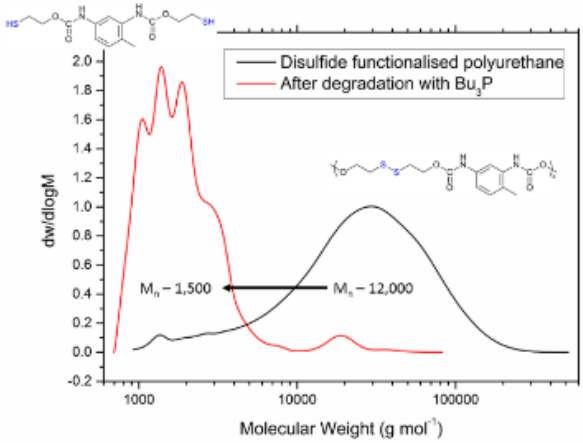

Figure 3 Reduction and degradation of disulphide functionalised polyurethane (blue trace) (Figure 2) using tributyl phosphine as the reducing agent down to thiol terminated oligomers (red trace)

There are multiple routes for the oxidation reaction to recombine the small dithiol containing compounds back to higher mass disulphide polymers, thus reforming the high mass polyurethane chains (Figure 1). Perhaps the simplest method is through bubbling with air, which can give rise to the recombination of the thiol groups.[24] However, in this work iron (III) chloride was used as an oxidising agent to accelerate the reaction.

, A large increase in molecular weight (M_n - 1,500 to 5,500 g mol^{-1}) was observed following the addition of $FeCl_3$, with the blue trace showing the mass distribution of the reformed polymer, Figure 4. This indicates that the small dithiol functionalised oligomers obtained from the degraded polyurethane recombined to form a higher mass linear polymer – thereby establishing a reversibly degradable system.

It is interesting that a small number of the short units shown after cleaving the linear chain remain and the polymer chain does not return fully to the original molecular weight. This

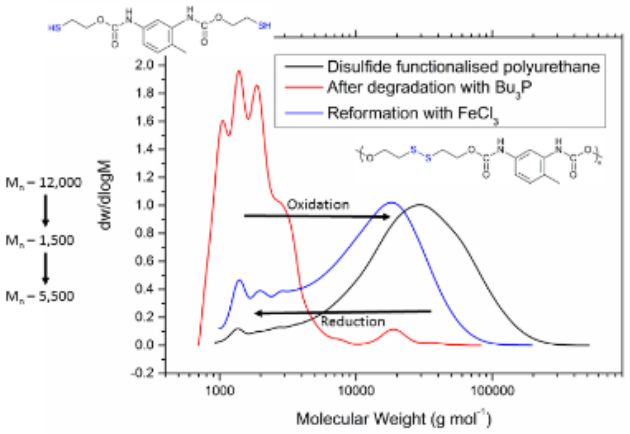

Figure 4 Reformation of the linear polyurethane (black trace) through oxidation with Iron (III) chloride as the oxidation agent from thiol terminated oligomers (red trace) released by the degradation of a disulphide functionalised polyurethane (blue trace)

indicates that either the reforming process is not as efficient as the cleaving process or that there is a loss of end group fidelity. However, the strong and distinct changes displayed in Figure 4 demonstrate the development of a reversibly degradable disulphide polyurethane material from readily available compounds using relatively mild redox reaction conditions.

Uretdione functionalised reversibly degradable polyurethanes

Uretdiones are primarily used in powder coatings to form crosslinked protective urethane coatings through urethane/biuret/allophanate reactions at high temperatures (≈200°C).[37] The use of uretdione functional groups as reversible covalent bonds seems to be understudied in polymer chemistry, with only a few open literature examples. The reaction of isocyanate groups with one another to form the uretdione linkage at low temperatures is carried out in the presence of a catalyst, which in itself gives strong temporal and thermal control (Figure 5). When diisocyanates are coupled in this way the resulting uretdione functionalised diisocyanate can be used for polyurethane formation.

The initial routes for the synthesis of a diisocyanate containing an uretdione reversibly cleavable linkage involved utilising a tributylphosphine catalyst at 0°C. Toluene diisocyanate (TDI) was coupled under these conditions to form a toluene diisocyanate dimer with a reversibly cleavable linkage (uretdione group) and two unreacted isocyanate groups on

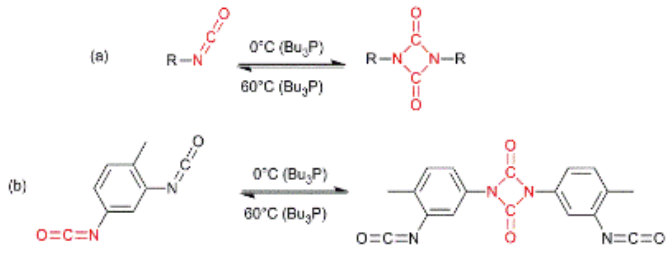

Figure 5 Examples of uretdione containing molecules (a) including the synthesis of an uretdione containing diisocyanate synthesised from two toluene diisocyanate molecules (toluene diisocyanate dimer) at 0°C with a Bu_3P catalyst (b).

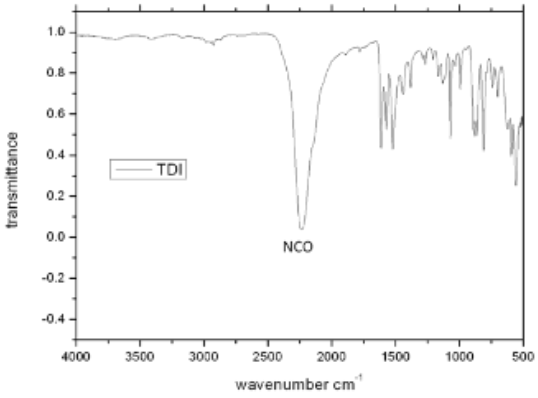

Figure 6 IR spectrum of toluene diisocyanate

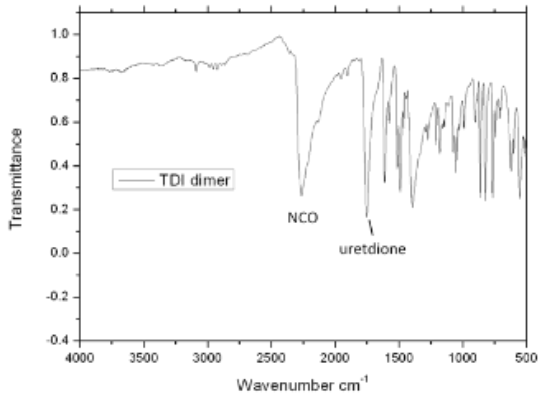

Figure 7 IR spectrum of toluene diisocyanate uretdione functionalised dimer

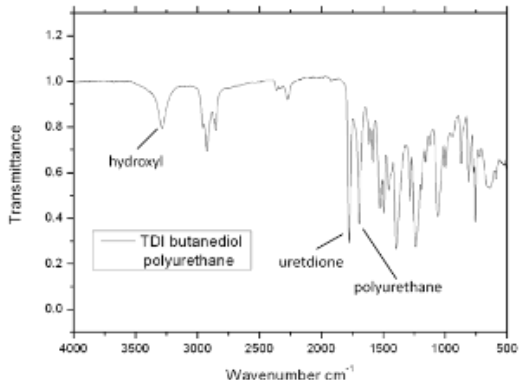

Figure 8 IR spectrum of an uretdione containing polyurethane synthesised from toluene diisocyanate dimer and butanediol with DBTDL at 40°C showing that uretdione group remains intact post polymerisation

either side with which further reactions, including a polymerisation with a diol, are possible (Figure 5).

The formation of the uretdione group can be conveniently followed through IR analysis at each step of the reaction. The IR spectrum of toluene diisocyanate, Figure 6, shows a strong isocyanate band located at 2,233 cm^{-1}. Upon cooling to 0°C in the presence of the phosphine catalyst the intensity of the isocyanate peak decreases and a peak at 1,755 cm^{-1} appears which corresponds to the uretdione group, indicating the successful synthesis of the toluene diisocyanate dimer (Figure 7). Precipitation of the dimer and the difference in reactivity

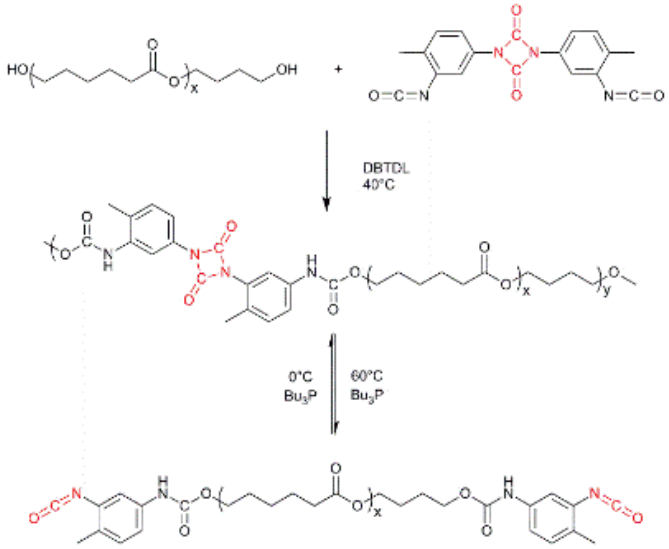

Figure 9 Synthesis of a thermoplastic polyurethane with uretdione cleavable functional groups (highlighted in red) throughout the polymer backbone formed from a polycaprolactone polyol and TDI dimer using DBTDL catalyst at 40°C

between the two isocyanate groups in toluene diisocyanate helps prevent further coupling reactions and keeps the product primarily in the form of a dimer.

The free isocyanate groups of the TDI dimer were reacted with a variety of diols, including several commercially available polycaprolactone polyols of various molecular weights (500, 2,000, 10,000 g mol^{-1}) and butanediol. The IR spectrum from the reaction with butanediol to form a polyurethane, Figure 8.

In the presence of a small excess of butanediol at 40°C with a DBTDL catalyst, the peak from the isocyanate group almost completely disappeared. The coincident appearance of both hydroxyl and polyurethane peaks is indicative of a successful polymerisation. Importantly, the uretdione peak remains, showing its relative stability under the polymerisation conditions (*i.e.* heat but no phosphine catalyst). Polyurethanes with cleavable uretdione linkages were also successfully prepared *via* a reaction of uretdione toluene diisocyanate dimer

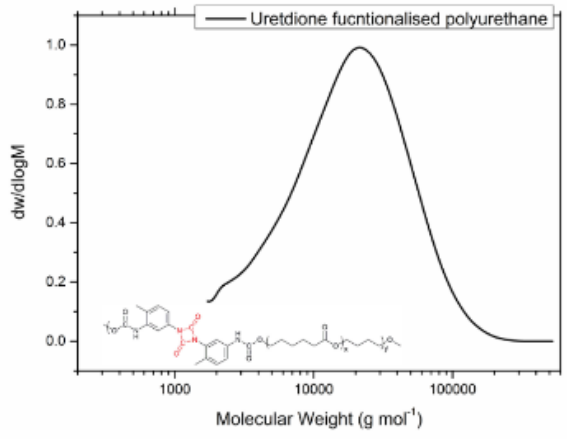

Figure 10 GPC trace of an uretdione polyurethane synthesised from M_n = 2,000 g mol^{-1} polycaprolactone diol and an uretdione functionalised TDI dimer reaction.

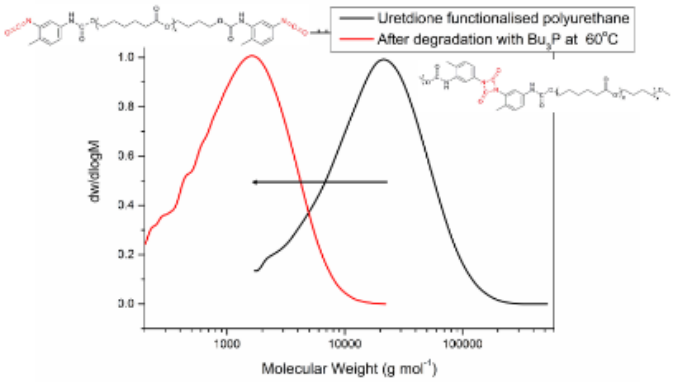

Figure 11 Overlay of GPC traces showing the successful synthesis of an uretdione functionalised polyurethane (black) followed by its degradation down to isocyanate functionalised polycaprolactone pre-polymers (red).The degradation was carried out at 60°C in the presence of Bu_3P catalyst

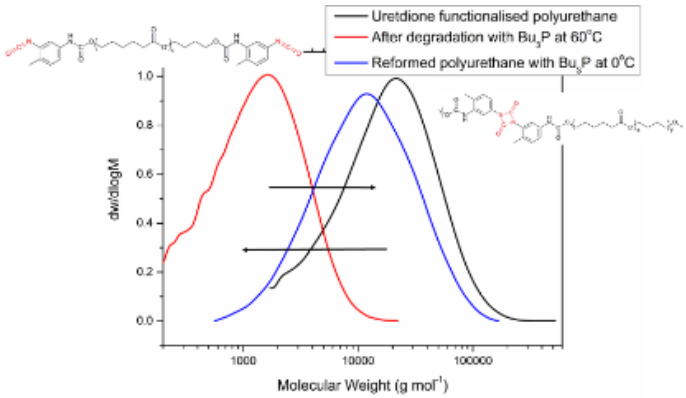

Figure 12 Overlay of GPC traces showing the successful synthesis of a uretdione functionalised polyurethane (black) followed by its degradation down to isocyanate functionalised polycaprolactone pre-polymers (red) and then successful reformation/rehealing of the polymer by the reformation of the uretdione bonds back to form a higher molecular weight uretdione functionalised polyurethane comparable to the original stating polyurethane (blue). The degradation was carried out at 60°C and the polymer reformed at 0°C both in the presence of a Bu_3P catalyst

with a M_n = 2,000 g mol^{-1} polycaprolactone polyol. Figure 9 shows the synthetic route using DBTDL as a catalyst at 40°C, and Figure 10 the GPC trace showing the successful formation of a thermoplastic uretdione functionalised polyurethane.

The polyurethane represented in Figure 10 was cleaved/degraded by heating to 60°C in the presence of tributylphosphine catalyst, releasing diisocyanate terminated polycaprolactone units (Figure 9) from the degradation of the uretdione bridges (M_w - 1,800 g mol^{-1}) (Figure 11 red trace).

The product of the degradation of the uretdione containing polyurethane, Figure 9, was cooled with ice to reform the uretdione groups from the exposed isocyanate groups, resulting in a polyurethane with an M_w -17,500 g mol^{-1} (Figure 12 blue trace). The formation back to a relatively high molecular weight indicates that there is a good retention of end group fidelity with respect to the free isocyanates, demonstrating the efficacy of the reversibility of this reaction. These results show the successful development of a novel reversibly degradable

polymeric system utilising uretdione chemistry. Being able to controllably reduce a polymer down to monomeric units and successfully reform the original polyurethane allows a novel route to controlling the physical properties of a polymer, as well as introducing reversible groups applicable to self-healing chemistry.

Combining uretdione and disulfide functionalised reversibly degradable polyurethanes

Thus far both reversibly degradable uretdione and disulphide containing polymer systems have been described. Both go through intermediate species before the reformation process and at this stage both have accessible reactive functional groups. These intermediates (proposed and described above) contain either reactive thiol or isocyanate groups released from their stable unreactive polymer chains.

As degradation requires similar reaction conditions for both disulphide and uretdione containing polymers, it was decided to attempt the cleavage of both polymers in the same reaction vessel (Figure 13). Once the thiols and isocyanates have been released there is the possibility of either reacting with the other in a non-reversible way, or to reversibly rebind back with themselves. Thus, following Le Chatelier's principle, this should result in the synthesis of a third, and unique, polymer – an AB alternating block copolymer with formation driven by the irreversibility of the cross coupling reaction (thiourethane formation). To the best of our knowledge, this idea of forming an alternating block copolymer by degradation of two different polymers in the presence of one another has not previously been reported.

The synthetic route illustrated in Figure 13 was explored using polyurethanes as described above. An uretdione functionalised polyurethane with a polycaprolactone polyol M_n - 2,000 g mol^{-1} soft segment and TDI dimer were dissolved with a disulphide functionalised polyurethane that was synthesised from TDI and 2-hydroxyethyl disulphide (Figure 14).

The disulphide and uretdione functionalised polyurethanes were degraded together in a one pot process in the presence of

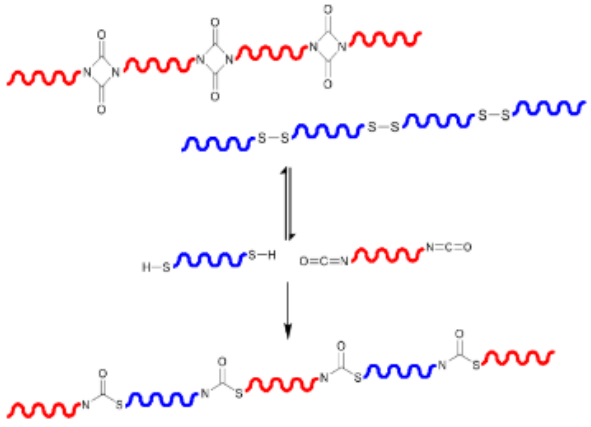

Figure 13 Schematic showing a synthetic route to an alternating block copolymer utilising uretdione and disulphide chemistries. Disulfide and uretdione containing polymers can be reversibly degraded to dithiols and diisocyanates. These can then react to form an AB alternating block copolymer.

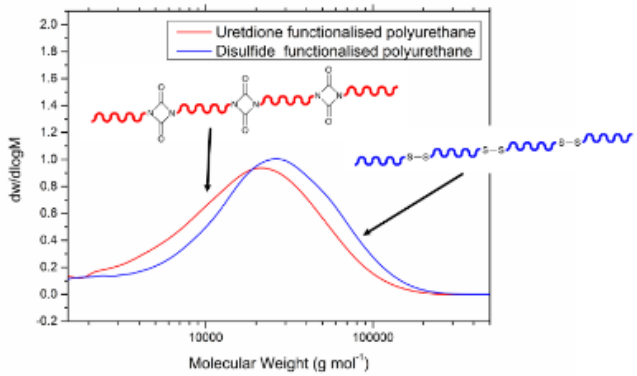

Figure 14 GPC overlays of uretdione functionalised polyurethane (Figure 18) (red trace) and a disulphide functionalised polyurethanes formed through the reaction of hydroxyethyl disulfide and TDI (blue trace)

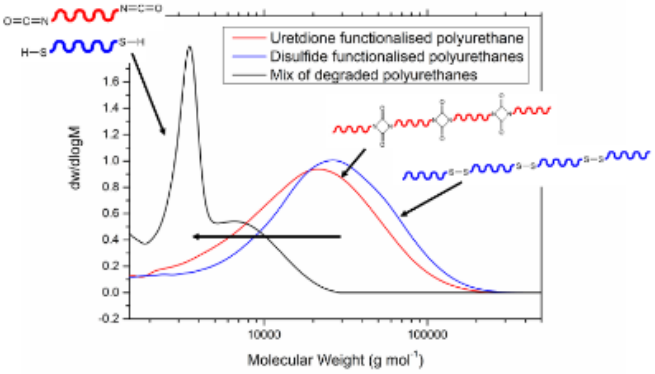

Figure 15 GPC trace (black) after degradation at 60°C with Bu_3P displaying a mix of smaller units from the cleaving of disulphide (blue) and uretdione (red) polyurethanes

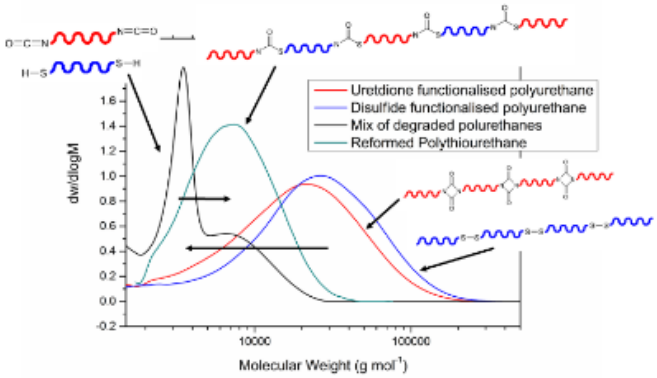

Figure 16 Showing the formation of a polythiourethane (green) from the degradation products (black) of disulphide (blue) and uretdione (red) functionalised polyurethanes

a tributyl phosphine catalyst at 60°C. A sample was taken for analysis after 1 hour (Figure 15) displaying the successful degradation of both polymers under these reaction conditions. The sharper lower molecular weight peak corresponds to the smaller, thiol terminated compounds from the degradation of the disulphide polyurethane and the higher molecular weight broader peak corresponds to the degraded uretdione

polyurethane containing isocyanate terminated M_w - 2,000 g mol^{-1} polycaprolactone pre-polymers.

Dibutyltin dilaurate was used as catalyst in order to promote the thiourethane reaction to form a third unique thiourethane polymer. The initial concentrations of the uretdione and disulphide polyurethanes require stoichiometric balance between the functional groups for successful formation of a high molecular weight thiourethane, which may explain the lack of a high molecular weight polythiourethane, Figure 16. The removal of the lower molecular weight species was successful and the appearance of a further polymer peak corresponding to the thiourethane was observed, Figure 16. This shows a novel route to forming these AB alternating block copolymers in situ from two A and B polymers.

Conclusions

This work describes two methods to incorporate reversibly cleavable functional groups throughout the backbone of polyurethanes to form reversibly degradable polymers. Both disulphide and uretdione rehealable polyurethanes have been synthesised under relatively mild conditions and the rehealability of these cleavable bonds proven. This process provides a method to control molecular weights, and therefore the properties of these materials, by applying different external stimuli.

Furthermore, the novel introduction of these two polymeric systems under the correct conditions has been shown to successfully degrade. Instead of individually reforming back to their respective polymers they form a third unique AB alternating block copolymer with non-degradable thiocarbamate linkages. This work describes a unique route to an AB alternating block copolymer. The original mixture of two polymers may have a dramatically different set of physical and chemical properties to the final product, and so this process may provide a route to vastly changing the properties of a polymeric material *in situ*.

A further aspect of this work is a way to form thiourethanes in a safer environment. Instead of working with thiols (strong smell) and isocyanates (high toxicity), the initial reactants are long chain disulphides and uretdiones which are considerably more stable and less toxic/odorous. There has already recently been a shift in the synthesis of polyurethanes away from isocyanates and polyols to transcarbamoylation for new environmental and safety requirements.[37]

Conflicts of interest

There are no conflicts to declare

Acknowledgements

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